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Cognition and Order in Langmuir-Blodgett Films of a 3-Hexadecyl Pyrrole and Ferrocene-Derivatized Pyrrole Mixed Monolayer System

L. Samuelson, A.K.M. Rahman, G.P. Puglia, S. Clough and S.K. Tripathy

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information content and 'intelligence'. Subsequently, materials may be prepared with widely varying electrical, optical, magnetic and structural properties. It is hoped that the processing of these materials into well ordered architectures will, in addition to optimizing these properties will also lead to smart devices, for example in chemical and biochemical sensing.

It has been determined that stable monolayer films of the mixed system could be formed at the air-water interface. The growth and assembly process led to polypyrrole 2-D lattices with heretofore unsurpassed order. In fact, the process of template polymerization leads to a new crystal phase for the polypyrrole component of the thin film structure. Various monolayer and multilayer films were prepared on platinum coated substrates for surface spectroscopic characterization using synchrotron radiation. Near Edge X-Ray Absorption Fine Structure studies revealed that highly ordered multilayer structures are being formed.

Cognition and Order in Langmuir-Blodgett Films of a 3-Hexadecyl Pyrrole and Ferrocene-Derivatized Pyrrole Mixed Monolayer System

L. Samuelson, A.K.M. Rahman, G.P. Puglia, S. Clough, S. Tripathy*
Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854 U.S.A.

T. Inagaki, X.Q. Yang, T.A. Skotheim
Division of Materials Science, Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973

Y. Okamoto
Department of Chemistry, Polytechnic University, Brooklyn, New York 11201

ABSTRACT

Novel, self-assembled materials have been designed and produced from first principle to possess unique structural hierarchy and electronic and optical properties. The Langmuir-Blodgett technique was used to study the molecular organization of a mixed 3-hexadecyl pyrrole (3HDP) and ferrocene-derivatized pyrrole (Fc-Py) surfactant system. The pyrrole moiety was chosen for its' well established electronic and optical properties when polymerized, while ferrocene, it is theorized, if properly oriented into a Langmuir-Blodgett monolayer film may show a layered array of transition metals which would be extremely valuable as a model for two-dimensional magnets. The ferrocene group may also provide the possibility of charge coupling between neutral ferrocene and oxidized ferricenium which could be controlled electrochemically or photochemically. The combination of these two moieties in a highly ordered molecular superlattice coupled with the ability to control the growth technique electrochemically, photochemically or by self-assembly should provide an effective means of directly controlling the material's information content and 'intelligence'. Subsequently, materials may be prepared with widely varying electrical, optical, magnetic and structural properties. It is hoped that the processing of these materials into well ordered architectures will, in addition to optimizing these properties will also lead to smart devices, for example in chemical and biochemical sensing.

It has been determined that stable monolayer films of the mixed system could be formed at the air-water interface. The growth and assembly process led to polypyrrole 2-D lattices with heretofore unsurpassed order. In fact, the process of template polymerization leads to a new crystal phase for the polypyrrole component of the thin film structure. Various monolayer and multilayer films were prepared on platinum

coated substrates for surface spectroscopic characterization using synchrotron radiation. Near Edge X-Ray Absorption Fine Structure studies revealed that highly ordered multilayer structures are being formed.

INTRODUCTION

An intelligent material may be defined as a material with enough information content to define its own organization and behavior, and which can further draw upon this organization the ability to perform and improve such intelligent functions as recognition. In the chemical sciences, this definition may be applied to, for example, a growing area of research interest: chemical sensors. Here, the ability to design and fine-tune a chemical system, which is quick to learn and detect the presence of specific desired species, suggests an infinite number of applications. In fact, advanced materials may be defined in which the molecules or "building blocks" have sufficient information content to dictate a structural hierarchy and order leading to specific functions as the components self-assemble.

In our laboratory, we have been developing a class of ordered electroactive materials from first principle. The desire is to build, in a complex hierarchy, a material with components that dictate their own assembly and this assembly provides the material with unique opportunities. Using the Langmuir-Blodgett technique, multilayer structures of 3-hexadecyl pyrrole and ferrocene-derivatized surfactant systems and mixtures thereof, have been observed to self-assemble into such a unique structural hierarchy which possesses novel functional behavior. The knowledge gained from the ability to process these materials into well-ordered organizations with controlled molecular architectures should allow for the full utilization of their unique electroactive properties.

In particular, it may be possible to employ these structures to form ultrathin electrodes and interconnects in multilayer superlattices where other optically and electronically active components are incorporated. In the case of the ferrocene-derivatized pyrrole system, it is theorized that such a highly structured hierarchy would show a layered array of transition metals which may be extremely valuable as a model for two-dimensional magnets. The ferrocene group may also provide electrochemical or photochemical control of the growth technique via charge coupling between the neutral ferrocene and oxidized ferricenium. As a result, materials may be prepared with widely varying electrical, optical, magnetic, and structural properties. This suggests that the processing of these materials into unique structural hierarchies could lead to the optimization of these properties and if fabricated onto suitable substrates, provide a means for chemical and biochemical sensing.

EXPERIMENTAL

The surfactant materials used in this investigation, 3-hexadecyl pyrrole (3HDP) and ferrocene-derivatized pyrrole (Fc-Py) were synthesized according to prescribed techniques[1]. Mixed monolayers of 3HDP and pyrrole, in a 1 to 500 ratio were prepared at the air-water interface using a commercial Lauda film balance. The monolayers were spread from chloroform solutions (concentration of 3HDP ca. 1-2 mg/ml) onto the subphase which contained an oxidizing solution of 0.01M $FeCl_3$. A Millipore Milli-Q purification system was used for subphase preparation and a constant temperature bath was used to control the subphase temperature. The mixed spreading solutions were dispersed at the air-water interface and then slowly compressed at speeds of about 5 $Å^2$ mol^{-1} min^{-1} to surface pressures of 10-15 mN/m prior to deposition.

Monolayers were transferred onto electron microscope grids for transmission electron microscopy and electron diffraction using both the horizontal and vertical dipping techniques. Multilayer assemblies were prepared onto platinum coated substrates for Near Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS) using the vertical dipping technique. A molecular modeling software package, "Quanta" from POLYGEN Inc., was used to theoretically predict the packing behavior of this system for the purpose of comparison to the experimental electron diffraction results.

In addition, monolayers of a Fc-Py surfactant system and mixed monolayers with 3HDP of various ratios were prepared on pure water subphases under similar conditions. Pressure-area isotherms were obtained for pure Fc-Py, 1:1, 1:2, 1:5, 1:10, and 1:20 ratios of Fc-Py to 3HDP. Monolayer and multilayer assemblies of the mixed systems were subsequently transferred onto platinum coated substrates for NEXAFS studies.

RESULTS AND DISCUSSION

500:1 Pyrrole to 3HDP

3-hexadecyl pyrrole (3HDP) was selected as a surfactant polypyrrole analog in an attempt to prepare monolayer films at the air-water interface and subsequently polymerize the pyrrole moiety into a highly ordered, two-dimensional, ultrathin, polypyrrole conductive film. Figure 1 shows the pressure-area isotherm of 3HDP at $20C^0$ on a pure water subphase. As indicated, 3HDP is a well-behaved system, with a relatively steep isotherm and area per molecule, at maximum surface pressure, of 22 $Å^2$.

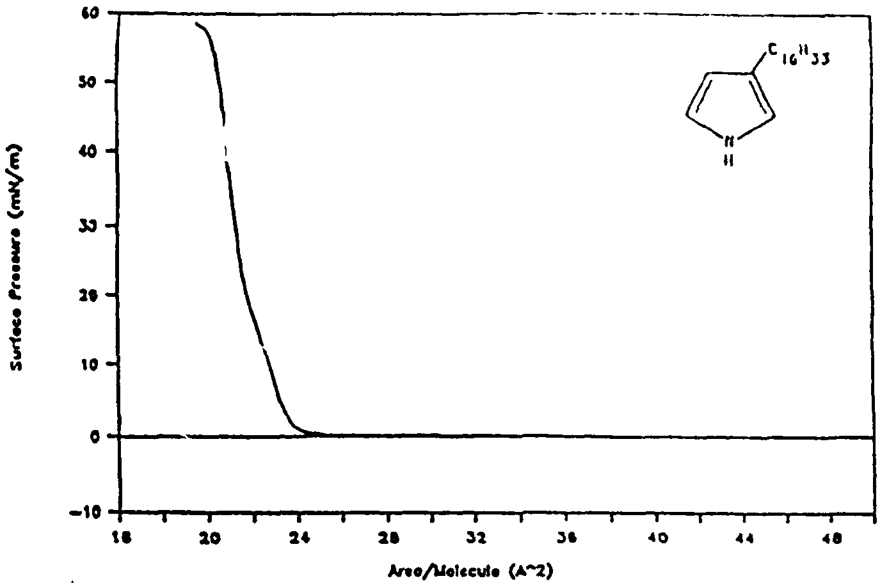

Figure 1. Pressure-area isotherm of 3HDP on a water subphase.

These results suggest that the molecules pack optimally into a vertical orientation as is typical of an ideal Langmuir-Blodgett system. In addition, the monolayer films are extremely stable as they may be annealed at constant pressure for long periods of time and allow facile deposition onto various substrates with good transfer ratios. Thus demonstrating, that the pyrrole ring of the 3HDP is sufficiently hydrophilic such that the deposition characteristics are those of a classic surfactive molecule.

However, it was previously reported [2] that , introduction of $FeCl_3$ into the subphase of the 3HDP monolayer, did not lead to polymerization to a sufficient extent through the pyrrole group. Instead, a premature buckling of the film was observed, simultaneously with an area expansion which was found to be dependent on the concentration of $FeCl_3$ in the subphase. In an attempt to explain this behavior one must consider the lowest energy conformation of the polypyrrole chain, which is a planar extended chain where the adjacent pyrrole rings point in the opposite directions to each other [3]. If all the pyrrole rings were to point in the same direction a helical structure would be generated. In the 3HDP monolayer the pyrrole rings are all expected to point in the same direction and it is possible to argue on kinetic grounds why polymerization through the pyrrole ring in such a monolayer structure may not occur. If pyrrole molecules could be inserted between adjacent 3HDP molecules so as to permit alternate pyrrole groups to point in opposite directions, kinetic restriction may be alleviated. Unfortunately, pyrrole is extensively soluble in water and a 1:1 ratio of pyrrole to 3HDP when deposited at the air-water interface does not ensure this preferred arrangement either. A much higher ratio, 500:1, of pyrrole to 3HDP spread on the subphase containing 0.1M $FeCl_3$ however leads to extensive polymerization and a

conductive film is obtained [4]. Alternatively, electrochemical polymerization in mixed multilayers of n-octadecane with surfactive pyrrole derivatives has been carried out by Shimidzu et al. [5]. It is possible, that the pyrrole groups from adjacent monolayers of a Y-type bilayer in this case provides the requisite configuration for an adequate polymerization condition.

Monolayers of 500:1 pyrrole to 3HDP were transferred onto electron microscope grids for transmission electron microscopy and electron diffraction. Electron micrographs were taken before and after washing with HCl to remove $FeCl_3$. The micrographs from the monolayers before washing with HCl indicate the possibility of inclusion of excess $FeCl_3$ from the subphase. A relatively thick texture also indicates the possibility of polymerization of the excess pyrrole in the subphase once polymerization is initiated at the air-water interface. Thus, we propose that pyrrole monomers may organize themselves at the air-water interface onto the template of a 1:1 3HDP to pyrrole layer.

Electron diffraction from the monolayers was done before and after washing with HCl. The "d" spacings of the sample before and after washing agree within 2-4 % experimental error, thus suggesting that the diffraction pattern is indeed resultant of the polymer and not of $FeCl_3$ inclusions. Further evidence was obtained by allowing a $FeCl_3$ aqueous solution to evaporate onto a carbon coated grid, upon which subsequent diffraction revealed completely different diffraction patterns. The diffraction patterns from 500:1 pyrrole to 3HDP were obtained and the corresponding experimental "d" spacings are shown in table 1. These "d" spacings do not conform to the hexagonal packing of the alkyl side chains nor do they agree with those reported by Geiss et al. [6] and Buckley et al. [7] for electrochemically polymerized polypyrrole. This well defined diffraction pattern is also not observed from a monolayer of 3HDP.

The "d" spacings for this polymer were also calculated assuming the lattice to be monoclinic. These calculated values are listed in table 1 for comparison, and are found to be in excellent agreement with the experimental values for a proposed monoclinic lattice with $a = 3.28$ Å, $b = 7.0$ Å, and $\gamma = 50^{o}$. These values are also close to one of the low energy packing structures for polypyrrole proposed by Orchard et al[8]. Orchard et al attempted to arrive at all the possible crystalline packing arrangements possible for polypyrrole. Interestingly, the crystal packing inferred for the polypyrrole part of the lattice in the present work mimics closely one of the monoclinic structures proposed in their paper. Theoretical crystal packing calculations were performed by us to recheck if our proposed packing is energetically feasible. Low energy packing arrangements close to the proposed structure were obtained using "Quanta" version 2.0, a molecular modelling software package developed by Polygen Corporation and installed on a Stellar GS1000 mini-supercomputer. Figure 2 is a schematic of the proposed packing of the Langmuir-Blodgett layer at the air-water interface.

TABLE 1

Experimental "d" spacings (Å)	Calculated "d" spacings (Å)
5.33	d_{010} = 5.36
2.57	d_{100} = 2.51
1.60	d_{220} = 1.60
1.35	d_{040} = 1.34
1.03	d_{330} = 1.06
0.90	d_{310} = 0.92
0.79	d_{440} = 0.80

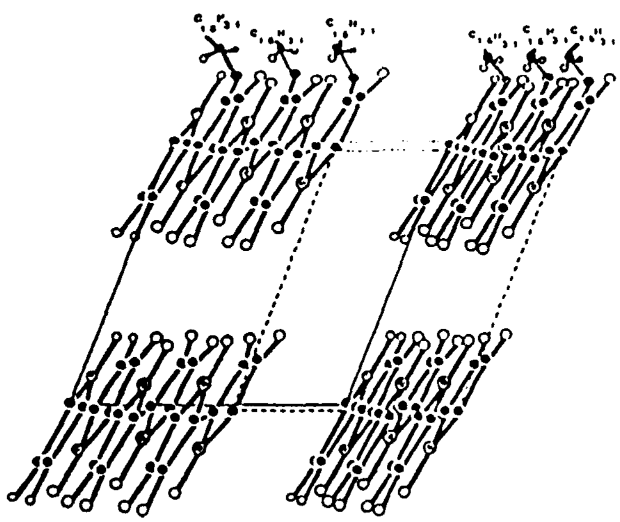

Figure 2. Schematic of the arrangement of polypyrrole chains at the air-water interface. Polymer chains are represented by the hexamer unit.

Thus, we conclude that the diffraction pattern obtained is from the polypyrrole produced at the air-water interface. Further, that this monolayer is in fact dictated into a new crystalline organization, as growth and polymerization is initiated from a 1:1

3HDP to pyrrole two-dimensional template, in which the horizontal lattice is comprised of electroactive polypyrrole. A continuation of this investigation next involves determining what effect the incorporation of a bulky ferrocene moiety will have on this unique structural hierarchy.

Fc-Py and 3HDP Mixed Monolayer System

The ferrocene-derivatized pyrrole (Fc-Py) molecule consists of a pyrrole group at one end of a 12 carbon aliphatic chain and a ferrocene group at the opposite end. It was hoped that this molecule which is structurally similar to the well-behaved 3HDP molecule would also form high quality monolayer films. However, this proved not to be the case. As shown in figure 3a, a pressure-area isotherm of the Fc-Py molecule on a pure water subphase, a stable monolayer is not being formed. The long plateau region and very low surface pressures are indication that the molecule is having difficulty packing on the water subphase. This is most likely due to the fact that both ends of the molecule are largely hydrophilic and the molecule has trouble preferentially orienting into a vertical arrangement.

To help stabilize this molecule and yet maintain the pyrrole moiety in the film, mixed monolayer systems were prepared using the well-behaved 3HDP molecule. It was hoped that the similarities between the two molecules would enable a homogeneous mixture to be formed as well as allow the 3HDP to assist the cumbersome Fc-Py to orient into the desired vertical arrangement. Mixture ratios of 1:0, 1:1, 1:2, 1:5, 1:10, and 1:20 of Fc-Py to 3HDP were prepared and characterized via pressure-area isotherms. As shown in figures 3b, 3c, and 3d (1:2, 1:5, 1:20 respectively), addition of 3HDP to the mixed system has a pronounced effect on the monolayer's properties. It was observed that with increasing amounts of 3HDP to the mixture, multiple transition regions developed and a corresponding decrease in length of the plateau region occurred. Also, a substantially steeper isotherm appears at smaller areas per molecule. These isotherms were found to be very reproducible and are indication that the 3HDP is optimizing the vertical orientation of the Fc-Py.

For further structural characterization, mono- and multilayer films of the various mixtures were transferred onto hydrophobic and hydrophilic (oxidized) platinum substrates. It was determined that higher surface pressures, (about 20mN/m) and higher ratio mixtures of 3HDP resulted in the most stable monolayers which could be transferred facilely onto the platinum substrates. Near Edge X-Ray Absorption Fine Structure (NEXAFS) techniques using synchrotron radiation were used to study the ordering of these Langmuir-Blodgett films at the molecular level[8]. Details of these measurements for the 500:1 pyrrole to 3HDP system have been reported elsewhere[8]. Figure 4 shows the NEXAFS spectra of a 4 layer film of 1:5, Fc-Py to 3HDP on a hydrophobic platinum substrate.

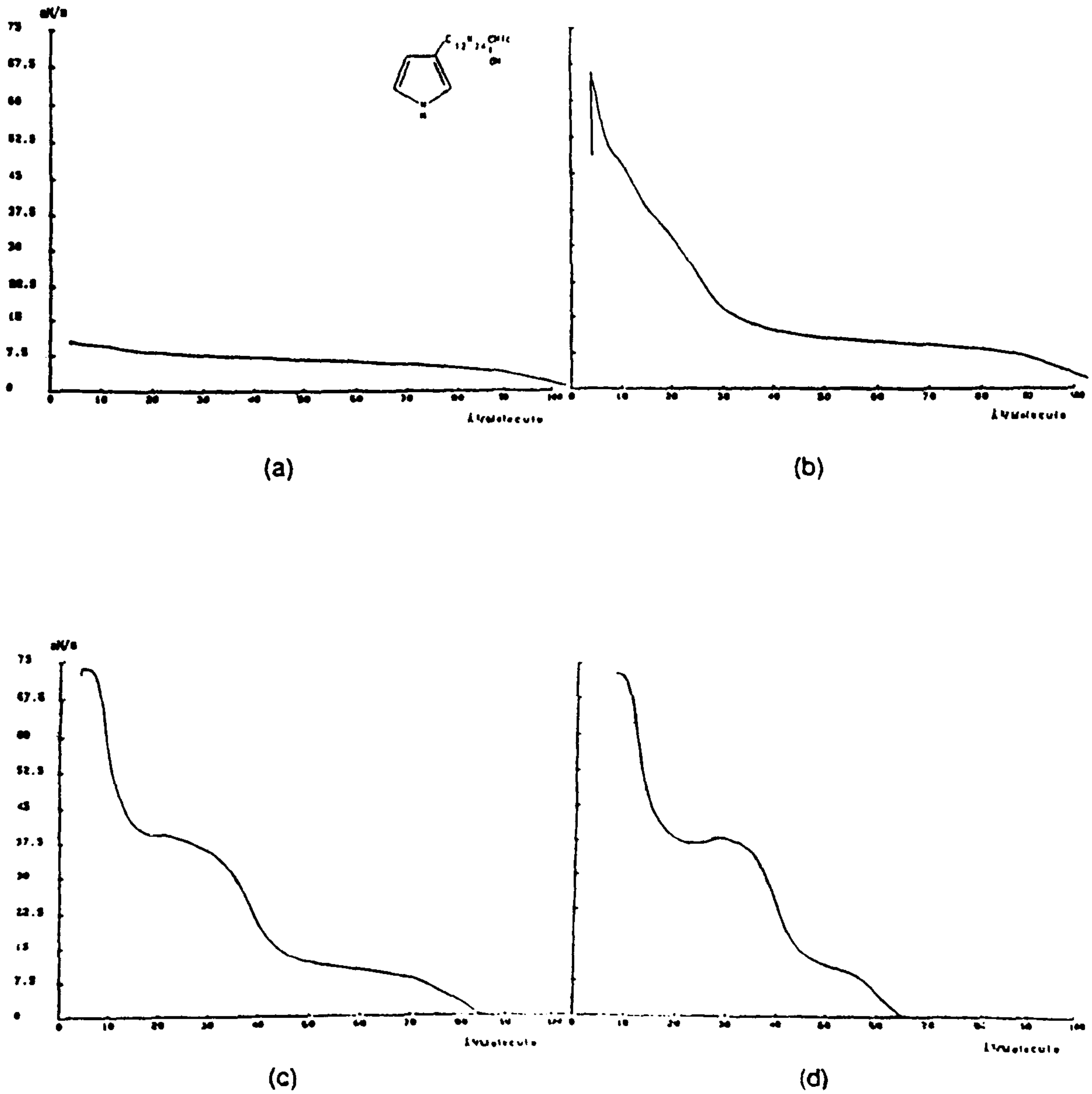

Figure 3. Pressure-area isotherms of mixtures of Fc-Py:3HDP on a pure water subphase

(a) 1:0 (b) 1:2 (c) 1:5 (d) 1:20

As observed, there is a marked dependence of the spectral features in the near-edge region on polarization. The carbon spectrum is predominately characteristic of the hydrocarbon chains in the multilayer since they contain the majority of carbon atoms. Thus, the strong polarization dependence of the spectrum suggests that the chains are

highly ordered. The sharp peak observed at approximately 290 eV corresponds to excitation to an empty orbital associated with the C-H bonds on the chain. This orbital is perpendicular to the chain direction, and its associated feature is most pronounced with the electric field vector parallel to the substrate. The broad peak observed at approximately 295 eV is assigned to the C-C bond which, on the average, is along the chain direction. This feature is most pronounced with the electric field vector normal to the substrate. Therefore, it may be concluded that the chains are highly ordered and oriented at an angle which approaches the normal to the substrate. Thus it appears, that a unique structural hierarchy is maintained when ferrocene moieties are incorporated into the films.

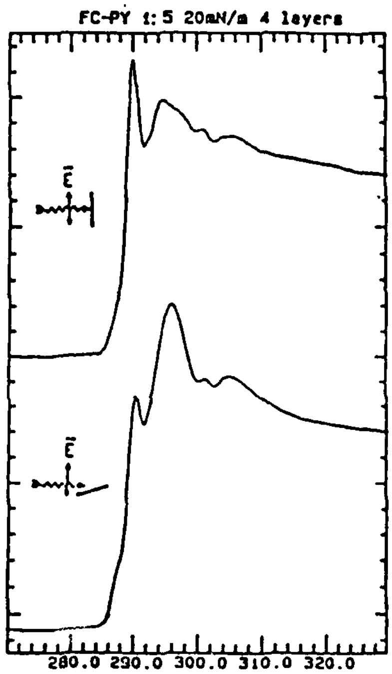

Figure 4. Carbon K-edge NEXAFS spectra of a 1:5 Fc-Py to 3HDP 4 layer LB Film on hydrophobic platinum.

CONCLUSION

The 3HDP/pyrrole mixed system has been shown to form large area thin films in a structural organization which is substantially different from bulk polymerized films. This organization is a direct result of confinement and controlled reaction in a two dimensional template at the air-water interface. An extension of these studies has included a mixed ferrocene-derivatized pyrrole and 3HDP system in an attempt to

combine the electroactive polypyrrole 2-D lattice with the unique electroactive and magnetic properties of ferrocene. It has been determined that this system is in fact able to self-assemble into a complex structural hierarchy. The anticipated electroactive properties of these films in conjunction with their anisotropy and complex architecture in multilayer lattices are expected to yield rich dividends as intelligent materials and are currently under investigation.

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